



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 31/22	A1	(11) International Publication Number: WO 99/04256 (43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14780 (22) International Filing Date: 16 July 1998 (16.07.98) (30) Priority Data: 60/052,674 16 July 1997 (16.07.97) US (71) Applicant (for all designated States except US): THE GOVERNMENT OF THE UNITED STATES OF AMERICA, represented by THE SECRETARY, DEPARTMENT OF HEALTH AND HUMAN SERVICES [US/US]; Suite 325, 6011 Executive Boulevard, Rockville, MD 20852 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MILLER, Dwight, W. [US/US]; 2901 Dan Road, Pine Bluff, AR 71602 (US). WILKES, Jon, G. [US/US]; 621 Cumberland #1, Little Rock, AR 72207 (US). CONTE, Eric, D. [US/US]; 1080 St. Andrews Circle, Bowling Green, KY 42103 (US). (74) Agent: MUELLER, Douglas, P.; Merchant, Gould, Smith, Edell, Welter & Schmidt, P.A., 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402-4131 (US).	(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: FOOD QUALITY INDICATOR DEVICE (57) Abstract A food quality indicator device comprising an indicator compound provided on a substrate. The indicator compound changes color due to the presence of volatile compounds, such as volatile bases, in spoiled food, even when the food is frozen. Alternatively, the indicator compound detects the presence of an unwanted amine-producing biological agent, such as bacteria or fungi. The indicator compound is typically contained within a polymeric matrix disposed on the substrate. Examples of suitable indicator compounds include halogenated azo dyes, sulfonated xanthene dyes, and sulfonated hydroxy-functional triphenylmethane dyes.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

FOOD QUALITY INDICATOR DEVICE

Field of the Invention

The present invention is directed generally to a device for indicating the quality of food. In particular, the present invention is directed to a device having
5 an indicator compound disposed on a substrate for colorimetrically indicating the quality of food, including frozen food.

Background

The determination of whether food has spoiled is of interest to a large number of people ranging from the food producer to the consumer, including
10 grocers, regulators, importers, exporters, and brokers. Many food products can spoil, including grains, fruits, and vegetables. However, one of the greatest areas of concern is spoilage of red meat, pork, poultry, processed meat products, and seafood. Spoiled foods pose many risks, chief among which is illness caused by consuming the food. Such illnesses may be life-threatening, especially for very young or very
15 old consumers, as well as persons with compromised immune systems.

Many foods are now packaged and/or frozen to retard spoilage. Unfortunately, packaged and frozen foods, which account for a large number of the available red meat, pork, poultry, processed meat, and seafood products, are harder to test for spoilage. Packaged food often needs to be unwrapped, examined, and
20 then repackaged if acceptable. Frozen food typically needs to be thawed in order to determine the quality of the food by current techniques, which often rely on color, smell, and texture. One method still used by the United States Food and Drug Administration for the testing of seafood is organoleptic analysis. This method requires thawing the seafood followed by an olfactory analysis by highly trained
25 experts to determine the condition of the food.

Devices for ascertaining the quality of frozen food, which do not require thawing the food, do exist. However, such devices are typically bulky and are not readily available and/or easily operated and interpreted by inexperienced individuals, such as consumers and grocers.

There is a need for a simple, quick, and effective device for determining the quality of food products to indicate if they are unsafe due to spoilage. In addition, there is a need for a device that can be packaged with food products which is effective in all typical food storage conditions, including
5 temperatures below 0°C. Such a device should be made of materials that are suitable for use with food products and do not contain or generate harmful chemicals. In addition, the device should provide indications of food quality that are easily read and understood by all or nearly all of the population.

Summary

10 The present invention is directed to a device that fulfills these needs. One aspect of the present invention is directed to an indicator device having a substrate and an indicator compound provided on the substrate. The indicator compound is colorimetrically responsive to volatile bases generated by food decomposition at temperatures below 0°C. Indicator devices can also be used to
15 detect other volatile compounds, including volatile acids.

Another embodiment of this aspect includes an indicator compound with a color transition within a range from about pH 1.0 to about pH 6.0. A further embodiment includes an indicator compound that is a halogenated xanthene dye, sulphonated azo dye, or a sulphonated hydroxy-functional triphenylmethane dye.
20 Another embodiment includes a polymeric matrix coated on the substrate, within which the indicator compound is held.

Another aspect of the invention is a method of making an indicator device, which includes forming a solution of an indicator compound, a solvent, and an acid. A silane monomer material is added to the solution. The solution is
25 disposed on a substrate and the silane monomer polymerizes to form a silica matrix in which the indicator compound is disposed.

Another aspect is a method of detecting spoilage in frozen food by providing an indicator device having a substrate and an indicator compound on the substrate. The indicator compound is colorimetrically responsive at temperatures
30 below 0°C to volatile bases generated by spoiled frozen food. The indicator device

and the indicator compound are exposed to the food and then the device is visually inspected to determine if the food is spoiled.

A further aspect is a food package for use with a food product. The food package includes packaging for a food product and an indicator device. The indicator device includes substrate and an indicator compound provided on the substrate. The indicator compound is colorimetrically responsive to volatile bases generated by food decomposition at temperatures below 0°C. The indicator device is associated with the packaging so as to be exposed to volatile bases emitted from the food product.

Another aspect is a method for detecting the presence of an unwanted amine-producing biological agent on a food product. An indicator device is exposed to the food product. The indicator device has a substrate and an indicator compound disposed on the substrate. The indicator compound is colorimetrically responsive to volatile bases emitted by the unwanted amine-producing biological agent. The device is visually inspected to determine if the food product contains the unwanted biological agent by observing if the indicator compound has changed color.

The above summary of the present invention is not intended to describe each illustrated embodiment or every implementation of the present invention. The figures and the detailed description which follow more particularly exemplify these embodiments.

Brief Description of the Drawings

The invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIG. 1 is a side perspective view of one embodiment of a food quality indicator device according to the present invention;

FIG. 2 is a side perspective view of another embodiment of a food quality indicator device that includes a shield layer according to the present invention;

FIGS. 3A-3D are top sectional views of an embodiment of a food quality indicator device according to the present invention, illustrating a method of obtaining quantitative or semiquantitative measurements of the food quality;

FIG. 4 is a side perspective view of a third embodiment of a food quality indicator device according to the present invention;

FIG. 5 is a side perspective view of the food quality indicator device of FIG. 1 mounted on a backing material according to the present invention;

FIG. 6 is a side perspective view of the food quality indicator device of FIG. 2 mounted on a backing material according to the present invention; and

FIG. 7 is a side perspective view of the food quality indicator device of FIG. 2 mounted within a groove of a backing material according to the present invention.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

Detailed Description of the Illustrated Embodiments

The present invention is believed to be applicable to a number of devices and methods for the colorimetric determination of food quality. While the present invention is not so limited, an appreciation of various aspects of the invention will be gained through a discussion of the devices and methods in connection with the detection of spoilage in red meat, pork, poultry, processed meat, and seafood products, and in particular, the detection of spoilage in seafood products, including both freshwater and marine fish and shellfish.

One embodiment of the present invention is illustrated in FIG. 1. A food quality indicator device 20 includes an indicator layer 22 disposed on a substrate 24. Substrate 24 is made from materials capable of supporting indicator layer 22, such as paper, plastic (e.g., polyester, polyethylene, polyvinyl chloride),

cotton, flax, resin, glass, fiber glass, or fabric. In some embodiments, indicator layer 22 is formed on the fibers of substrate 24. Substrate 24 may have a variety of shapes and forms. For example, substrate 24 may be a strip, a sheet, or a string. In some embodiments, substrate 24 is part of food packaging material or is adhered to food packaging materials. The thickness of substrate 24 may vary. For substrates that readily absorb the chemicals in indicator layer 22, the thickness of the substrate may be limited in some embodiments to reduce the amount of absorbed chemicals.

Indicator layer 22 typically includes a polymeric matrix and one or more indicator compounds held within the matrix. The indicator compounds are usually dye compounds capable of colorimetrically indicating the presence of one or more chemical compounds associated with the decomposition or spoilage of food. In particular, the indicator compounds are capable of indicating the presence of decomposition products at temperatures below the freezing point of water. In this case, the indicator compounds should be responsive to decomposition compounds in the absence of water mediation.

There are a number of chemical compounds that are generated as food decomposes and spoils. Many foods that contain substantial amounts of protein materials, including red meat, pork, poultry, processed meat, and seafood products, generate volatile compounds, such as volatile bases, during decomposition. Amines comprise one group of volatile bases generated by decomposing food through processes such as the deamination of free amino acids and the degradation of nucleotides. Among the generated amines are ammonia, dimethylamine, and trimethylamine. Dimethylamine and trimethylamine are at least partially volatilized even in frozen food. Other amines associated with decomposing food include histamine, cadaverine, putrescine, indole, spermine, and spermidine. These compounds may also volatilize. These and other compounds comprise the total amount of organic bases formed during the decomposition of food.

In general, the indicator compound in indicator layer 22 changes colors in the presence of these volatile bases. The particular range of concentrations of volatile bases that will cause a color change of the indicator compound depends on factors such as the particular indicator compound used in the device, the chemical environment in which the indicator compound is placed (e.g., the acidity or basicity

of the environment), and the amount of indicator that is used in the device. The appropriate range can be determined for each food product by, for example, calibration with test samples. It is expected that different food products will produce different amounts of volatile bases when spoiled. However, food products that are similar (e.g., different types of fish) may generate similar amounts of volatile bases.

The range of concentrations of generated volatile bases that cause a color change in the indicator compound may be chosen to indicate a variety of conditions. For example, the color change may indicate that the food is unsafe for consumption or that the food will soon become unfit for consumption.

In other embodiments, the presence of an unwanted amine-producing biological agent, such as bacteria or fungus, may be detected instead of or in addition to food decomposition. A color change of the indicator compound may indicate the presence of an unwanted biological agent, such as bacteria or fungi. For example, certain fungi generate amines when in contact with grains. In particular, smut on unprocessed wheat stored in silos or in cargo holds of ships generates trimethylamine. Although, the invention is described herein with reference to the detection of food decomposition, it will be appreciated that the same devices, methods, and principles can be applied to the detection of unwanted biological agents.

Indicator compounds for use in the present invention typically have a color change in a range from about pH 1.0 and about pH 6.0, and preferably in a range from about pH 2.5 and pH 5.0, in aqueous solution. Ideal indicators are non-toxic and, preferably, can be used as food additives or dyes, thereby minimizing any danger that might occur if the indicator compound leaks from the food quality indicator device. Preferably, the indicator compounds are approved by a regulatory agency, such as the U.S. Food & Drug Administration, for use with food products. In addition, the ideal indicators have a strong color change upon detection of the volatile bases and the color change is apparent even to color blind members of the population. However, indicators without these particular characteristics may also be used.

Indicators for use in the food quality indicator device should be capable of changing colors at temperatures below the freezing point of water. This

means that the colorforming chemical reaction of the indicator with the volatile bases emitted by the decomposed food does not rely on mediation by water. Many commercial pH indicator strips state in their instructions that the strip must be placed in contact with an aqueous solution and read while wet. Experiments using these strips, detailed hereinafter, indicate that the strips do not respond appropriately to bases emitted by spoiled frozen fish.

Classes of suitable indicators include xanthene dyes, azo dyes, and hydroxy-functional triphenylmethane dyes. A number of these indicators contain phenol functionalities. Many suitable indicators are halogenated and/or contain acidic functional groups, such as $-\text{COOH}$, $-\text{SO}_3$, or $-\text{S}(\text{O}_2)\text{O}-$ or salts thereof. Preferred indicators include halogenated xanthene dyes such as Phloxine B, Rose Bengal, or Erythrosine; sulfonated azo dyes such as Congo Red and Metanil Yellow; and sulfonated hydroxy-functional triphenylmethane dyes such as Bromophenol Blue, Bromocresol Green, and Phenol Red. The most preferred indicators for use with frozen seafood are Phloxine B, Rose Bengal, and Bromophenol Blue.

The indicator compound is typically held within a polymeric matrix to prevent leakage of the indicator compound into the food. The polymeric matrix may be adapted to clathrate the indicator compound. Suitable polymeric matrices are at least partially permeable to one or more of the volatile bases to be detected. Preferably, the polymeric matrix is also water-repellent, non-toxic, transparent, and made from reagents suitable, and preferably approved, for use with food or food packaging materials. Examples of such polymeric matrices include matrices made from silicone polymers including polydimethyl silicones, silane titanium oxide sol-gels, silane cross-linkable resins, polyvinylchloride, and butylated cellulose.

One particularly useful polymeric matrix is a sol-gel glass formed by hydrolysis of one or more alkoxysilanes. Suitable alkoxysilanes include tetraalkoxysilanes and alkyl trialkoxysilanes, where the alkyl group is a C1 to C30 straight or branched-chain alkyl group and the alkoxy group is a C1 to C4 alkoxy group. Examples of suitable alkoxysilanes include tetramethoxysilane, tetraethoxysilane, alkyl trimethoxysilane, and alkyl triethoxysilane.

Generally polymerization of the alkoxysilanes may be acid or base catalyzed, typically in the presence of water. Useful catalysts of this polymerization

reaction include high-volatility acids such as hydrochloric acid, acetic acid, formic acid, or trifluoroacetic acid.

Indicator layer 22 may also include other additives such as a polymeric resin, hydrated alumina, or a non-volatile acid. The polymeric resin may be added to increase the strength or stiffness of the polymeric layer. One example of a suitable resin is polyvinyl alcohol (PVA) with an average molecular weight of about 5,000 to 20,000.

Hydrated alumina can be added to help retain the volatile bases on the indicator device. This may provide additional stability to the color change observed with the strip, thereby making the color change irreversible or slowly reversing. One example of suitable hydrated alumina compounds with demonstrated use in the present invention is zeolites. Zeolites are well-known for their ability to retain molecules, like ammonia.

Non-volatile acids may be added to control the rate of response or the detection sensitivity of the food quality indicator device. While no particular theory is integral to the invention, it is thought that the acid may alter the acid loading of the polymeric matrix, thereby altering the amount of volatile base that is needed to cause the indicator compound to change color. Suitable acids include concentrated sulfuric acid, sulfamic acid, phosphoric acid, zeolites, alumina, polyacrylic acid, and a sulfonated perfluoroethylene, such as Naphion®-H.

Typically, indicator layer 22 is applied to substrate 24 before or during the polymerization of the polymeric matrix to provide good adhesion of the indicator layer to the substrate. Application of indicator layer 22 to substrate 24 may be accomplished by a variety of techniques including dipping the substrate in the solution, spraying the solution on the substrate, brushing the solution onto the substrate, or pouring the solution over the substrate. In one embodiment, the indicator layer is applied so that the indicator layer forms a letter, number, or symbol that becomes apparent or changes color in the presence of spoiled food. In another embodiment, the substrate or an optional backing material is colored to provide additional contrast for the color change of the indicator compound. For example, the substrate or optional backing material may be white. Alternatively, the substrate or optional backing material may have a color similar to the color of the indicator prior

to exposure to spoiled food. The color change of the indicator compound can then be contrasted with the color of an adjacent portion of the substrate or optional backing material that is not covered by the indicator layer.

FIG. 2 illustrates another embodiment of the invention in which the indicator layer 22 and substrate 20 are surrounded by a shield layer 26. Shield layer 26 may be attached to indicator layer 22 and/or substrate 24 by a variety of methods including *in situ* polymerization, heat sealing, ultrasonic welding, or adhesive attachment.

In one embodiment, shield layer 26 is an amine permeable, water repellent polymer that serves to protect the underlying indicator layer from damage and/or further prevents leakage of the indicator compound from the device. This shield layer may be made of the same material as the polymeric matrix of the indicator layer, but other polymers are also acceptable. Suitable polymers for use in this type of shield layer include silica sol-gels, silicone polymers including polydimethyl silicones, silane titanium oxide sol-gels, silane cross-linkable resins, polytetrafluoroethylene (e.g., TeflonTM), polyvinylchloride, or butylated cellulose. The shield layer is typically about 10 to 100 μm thick so that the amount of amine vapor reaching the indicator layer is not reduced below detectable levels.

In another embodiment, shield layer 26 is impermeable to amine vapors. This shield layer may also be water repellent, non-toxic, transparent, and/or made from reagents that are appropriate for use with food packaging. Suitable polymeric materials for this type of shield layer include polypropylene, polyethylene, polystyrene, and copolymers of polystyrene such as ABS (a copolymer made from acrylonitrile, butadiene, and styrene monomers) or poly(styrene-butadiene).

One exemplary embodiment of the invention having the amine-impermeable shield layer is illustrated in FIG. 3A (in which the relative difference in size between the shield layer 26 and indicator layer 22 has been exaggerated for illustrative purposes). The illustrated embodiment is an indicator strip 25 that can be used to provide a quantitative or semiquantitative measure of the food quality. Indicator strip 25 is similar to the embodiment illustrated in FIG. 2 with a shield layer 26 surrounding an indicator layer 22 and a substrate 24. To use the indicator

strip, a portion of shield layer 26 is removed to expose a portion of indicator layer 22 to vapors from the food. One method for removing the portion of the shield layer is to cut away a portion 27 of the strip as shown in FIG. 3B, thereby exposing an edge 28 of indicator layer 22. As volatile bases from the food contact the exposed edge of the indicator layer, the indicator compound 30 at that edge changes color, as illustrated in FIG. 3C. The color 32 diffuses through the indicator layer with increased exposure to the volatile bases, as depicted in FIG. 3D.

Quantitative or semiquantitative measurements can be made using this strip by measuring the distance that the color diffuses over a predetermined time period at a particular temperature. In one embodiment, the food quality indicator device includes markings spaced at intervals to provide a convenient way for measuring the depth of the diffused color. Measurements of color diffusion can be compared to calibration samples to determine the quality of the food.

To obtain quantitative or semiquantitative measurements, the amount of indicator compound and the size of the exposed edge should be proportional to the weight of food in the container. Typically, samples of different types of food can not be compared, however, foods that are sufficiently similar (e.g., different types of fish) may yield comparable results, other factors being equal.

Another embodiment is illustrated in FIG. 4 in which two indicator layers 22a, 22b are disposed on one or more substrates 24a, 24b. Only indicator layer 22b is surrounded by an amine-impermeable shield layer 26b. Indicator layer 22a can be compared to layer 22b to determine when a color change has occurred due to the presence of volatile bases. Indicator layer 22b is prevented from changing color because of shield layer 26b. Comparison of the two indicator layers 22a, 22b provides a convenient method for determining when an indicator compound has changed color, especially when the color change is subtle or slight. Other configurations are possible.

FIG. 5 illustrates an embodiment of the invention in which indicator device 20 is provided on a backing material 30 that can be attached to food packaging. The attachment of backing material 30 to the packaging may be accomplished, for example, via an adhesive layer 32 applied to the backing material 30 or by bonding the backing material to the packaging using a curable resin or other

bonding agent. Device 20 may also include an adhesive protection layer (not shown) manufactured with the device and taken off to expose the adhesive for application to packaging material or any other desired place. Device 20 is attached to backing material 30 by methods that include heat sealing or adhesive attachment.

5 Device 20 may cover all or only a portion of backing material 30.

In another embodiment, device 20 is directly attached to food packaging via an adhesive or other method. In a further embodiment, indicator layer 20 is directly formed on food packaging material, using the packaging material as a substrate.

10 FIGS. 6 and 7 illustrate two embodiments similar to that of FIG. 5 except that an amine-impermeable shield layer 26 is applied over indicator layer 22. The embodiment depicted in FIG. 6 shows an indicator device 20 on a backing material 30. A shield layer 26 is applied over device 20 and backing material 30 to prevent amine vapor from contacting the device except in a region from which the
15 shield layer has been removed. Alternatively, device 20 may be constructed with a shield layer and then attached to backing material 30.

FIG. 7 shows a groove 34 into which device 20 is placed. An amine-impermeable shield layer 26 is then applied over device 20 and the raised portions of backing material 30 which define groove 34. Alternatively, shield layer 26 is
20 formed over device 20 prior to placement of the device in groove 34.

The embodiments of FIGS. 6 and 7 may be manufactured with regions of device 20, such as an edge of the device, uncovered by shield layer 26. Alternatively, a portion of shield layer 26 may be removed (e.g., cut away) when the device is to be used.

25 Another embodiment of the invention includes two or more strips or strings, preferable positioned adjacent to each other. Each of the strips or strings contains a different formulation of the indicator compound and other additives to provide different sensitivities. For example, the formulation may differ by the amount of indicator compound or by the amount of acid added to the indicator
30 compound. Typically, the two or more strips or strips are coated with a non-permeable coating.

In operation, the non-permeable coating is removed from an end of each of the strips or strings, as described above. A quantitative analysis of the contaminant can be determined by comparing the relative lengths of the strips or strings with altered color for a given period of time. These relative amounts, for example, can be compared to test samples for qualitatively or quantitatively determining the amount of contamination of the food.

Although at least some embodiments of the invention can be used to detect contamination in frozen food and at temperatures below 0°C, these same or other embodiments may be used to determine contamination at higher temperatures. For example, a bag containing a food sample and an indicator device may be heated, for example, boiled in water, to increase the emission rate of contaminants from the sample. In any case, the indicator device operates without water mediation, for example, in a sealed bag. Heating the food and the indicator device may decrease the amount of time required for detection of contamination.

One embodiment of a method for forming a food quality indicator device is to dissolve an indicator compound in water, methanol, ethanol, propanol, acetone, ether, or other indicator solvating liquid to provide a 0.01 to 1.0 mg/mL solution. About 1-10 mL of 0.01-1.0 M high-volatility acid, such as hydrochloric acid, acetic acid, formic acid, or trifluoroacetic acid is added to 50 mL of the indicator solution. 0-10 grams of a polymeric resin capable of dissolving in the solvent, 0-10 grams of hydrated alumina, and 0-10 grams of a non-volatile acid, such as phosphoric acid, are optionally added to the indicator solution.

In a separate container, 1-50 grams of a tetraalkoxysilane and 1-50 grams of an alkyl trialkoxysilane are mixed. The silane mixture is then added to the indicator/acid solution. This initiates the silane polymerization. At least a portion of the solution is then applied to the substrate before the silane polymerization is complete. The device is allowed to dry. Heating may be used to accelerate drying. Optionally, the device is then encased in a shield layer formed, for example, by polymerization of monomer materials around the layer or by application of one or more polymer films.

Although the invention has been exemplified with respect to the detection of volatile bases, such as amines, it will be understood that other volatile

compounds, including, for example, volatile acids, such as H₂S or mercaptans (i.e., thiols), can also be detected by the same or similar indicator devices. These volatile compounds, including volatile acids, may be generated, for example, by decomposition of food or by the presence of biological agents.

5 In particular, an indicator device can be formed using an indicator layer that changes color in the presence of a volatile acid. For example, an indicator compound may be used that produces a color change in a range from about pH 8 to about pH 14, preferably, in a range from about pH 9 to about pH 13, in aqueous solution. The indicator compound, should be capable of changing colors at
10 temperatures below the freezing point of water and/or without mediation of water.

A polymeric matrix may be formed using, for example, a sol-gel glass formed by base catalyzed polymerization of alkoxysilanes. Preferably, the base is volatile. In addition, a non-volatile base may be disposed on the substrate of the indicator device to control the rate of response and/or detection sensitivity of the
15 indicator device.

EXAMPLES

The following examples demonstrate methods for the manufacture and use of the food indicator strips of the invention. It is to be understood that these
20 examples are merely illustrative and are in no way to be interpreted as limiting the scope of the invention.

Example 1

Preparation of a Food Quality Indicator Device

25 using Bromophenol Blue

50 mg of bromophenol blue were dissolved in 50 mL of ethanol. Five mL of 0.1 M HCl and five grams of polyvinyl alcohol (M.W. 2000) were added to the ethanol solution. Five grams of tetraethoxysilane and five grams of octadecyltriethoxysilane were mixed in a separate container. The silane mixture was
30 then added to the ethanol solution with mechanical stirring. Paper strips and string were dipped into the solution and allowed to dry. After drying, the paper strips and string were coated with polyvinyl chloride (PVC) dissolved in tetrahydrofuran

(THF). The THF was allowed to evaporate and the paper strips and strings were then laminated between two polypropylene films to form an amine-impermeable, transparent shield layer.

One edge of a strip and an end of a string were cut to expose the
5 bromophenol blue indicator layer to a known spoiled cod sample at -20°C for a period of one hour. Both the strip edge and the string end showed a dramatic color change from yellow to blue within the exposure period. The color change was also noticeable on a region of the strip and string adjacent to the open edge/end. This indicated that the volatile bases had diffused into the indicator device through the
10 open edge/end.

Example 2

Preparation of a Food Quality Indicator Device using Phloxine B

15 a) Indicator strips and strings were made as described in Example 1 except that Phloxine B was used as the indicator and the PVC coating was not applied. In this case, the color change was from colorless or slightly pink to bright fuchsia (i.e., pinkish red) after one hour exposure to the frozen spoiled cod sample.

b) Another set of indicator strips and strings was made. For this set,
20 a hydrated alumina solution was made by stirring 10 grams of alumina in 50 mL of 1.0 M HCl for 15 hours at room temperature. 50 mg of Phloxine B was dissolved in 50 mL of ethanol and 5 mL of the hydrated alumina solution. Five grams of tetraethoxysilane and five grams of octadecyltriethoxysilane were mixed in a separate container. The silane mixture was then added to the ethanol solution with
25 mechanical stirring. Paper strips and string were dipped into the solution and allowed to dry. After drying, the paper strips and string were laminated between two polypropylene films which formed an amine-impermeable, transparent shield layer.

One edge of a strip and an end of a string were cut to expose the Phloxine B indicator layer to a known spoiled cod sample at -20°C for a period of
30 one hour. Both the strip edge and the string end showed a dramatic color change from colorless or slightly pink to bright fuchsia (i.e., pinkish red) within the exposure period. The color change also was noticeable on a region of the strip and string

adjacent to the open edge/end. This indicated that the volatile bases had diffused into the indicator device through the open edge/end. However, the length of the color change was considerably shorter than for the Phloxine B strips and string described in a), possibly due to absorption of the volatile bases by the hydrated alumina in the indicator layer. This illustrates one way of controlling sensitivity of the food quality indicator device as the hydrated alumina may retard diffusion and reversibility of the color change.

Example 3

Preparation of another Food Quality Indicator Device using Phloxine B

Indicator strings were made. First, a hydrated alumina solution was made by stirring 10 grams of alumina in 50 mL of 1.0 M HCl for 15 hours at room temperature. In addition, two grams of polyacrylic acid were suspended in 100 mL of ethanol. 15 mg of Phloxine B and 0.285 mg of phosphoric acid were dissolved in 50 mL of ethanol, 5 mL of the hydrated alumina solution, and 5 mL of the polyacrylic acid suspension. Five grams of tetraethoxysilane and five grams of octadecyltriethoxysilane were mixed in a separate container. The silane mixture was then added to the ethanol solution with mechanical stirring. Polyester string was dipped into the solution and allowed to dry. After drying, the string was covered by TeflonTM-spray (PTFE Release Agent Dry Lubricant MS122N/CO2 from Miller-Stevenson, Sylmar CA).

One edge of a strip and an end of a string were cut to expose the Phloxine B indicator layer to a known spoiled cod sample at -20°C for a period of one hour. Both the strip edge and the string end showed a dramatic color change from colorless or slightly pink to bright fuchsia (i.e., pinkish red) within the exposure period. The color change also was noticeable on a region of the strip and string adjacent to the open edge/end. This indicated that the volatile bases had diffused into the indicator device through the open edge/end.

Comparative Example**Exposure of Commercial pH Indicator Strips
to a Spoiled Cod Sample at -20°C**

Commercial pH papers were exposed to the spoiled cod sample of
5 Examples 1 and 2 at -20°C for one hour just as the food quality indicator strips of
Examples 1 and 2. The pH papers tested were a) ColorpHast™ pH 3.5-4.5 paper
from EM-Reagents (Cat. No. 9581), b) pH Test Strips 0-14.0 from Sigma Chemical
Company (Cat. No. P4786), and c) Alkacid Test Paper from Fisher Scientific Co.
(Cat. No. 14-839) with a range from pH 2 to 10. Paper a) showed a slight darkening
10 in color, going from orange to orange-red, upon exposure to the sample, however the
color reverted back to orange after 60 seconds at room temperature. Similarly, paper
b) showed a slight darkening of one color region, going from olive brown to a
slightly darker hue, which reverted after 5 minutes at room temperature. There was
no observed change in the color of pH paper c).

15 In contrast, the food quality indicator devices of Examples 1 and 2
had dramatic color changes, blue to yellow for the Bromophenol Blue indicator
device and colorless or slightly pink to bright fuchsia for the Phloxine B indicator
device. In each case, the color change was permanent or lasted at least several
weeks at room temperature after removal from the amine-containing environment.

20

The present invention should not be considered limited to the
particular examples or embodiments described above, but rather should be
understood to cover all aspects of the invention as fairly set out in the attached
claims. Various modifications, equivalent processes, as well as numerous structures
25 to which the present invention may be applicable will be readily apparent to those of
skill in the art to which the present invention is directed upon review of the present
specification. The claims are intended to cover such modifications and devices.

WHAT IS CLAIMED IS:

1. An indicator device, comprising:
a substrate; and
an indicator compound disposed on the substrate, the indicator compound being colorimetrically responsive at temperatures below 0°C to volatile bases generated by food decomposition.
2. The device of claim 1, wherein the indicator compound comprises a compound with a color transition in a range from about pH 1.0 and about pH 6.0.
3. The device of claim 2, wherein the indicator compound comprises a compound with a color transition in a range from about pH 2.5 and about pH 5.0.
4. The device of claim 1, wherein the indicator compound comprises a compound with one or more acidic functional groups in the absence of amino or alkylamino functional groups, wherein at least one of the one or more acidic functional groups is -COOH, -SO₃, -S(O₂)O-, or salts thereof.
5. The device of claim 1, wherein the indicator compound is a halogenated xanthene dye, a sulfonated azo dye, or a sulfonated hydroxy-functional triphenylmethane dye.
6. The device of claim 5, wherein the indicator compound is Bromophenol Blue, Phloxine B, Rose Bengal, Congo Red, or Metanil Yellow.
7. The device of claim 1, wherein the device further comprises a first polymeric matrix coated on the substrate and the indicator compound is disposed within the first polymeric matrix.
8. The device of claim 7, wherein the first polymeric matrix comprises a silicon-containing matrix.

9. The device of claim 1, wherein the first polymeric matrix is formed by an acid catalyzed polymerization of a monomer material.
10. The device of claim 9, wherein the monomer material comprises a tetraalkoxysilane, an alkyl trialkoxysilane, or a mixture thereof.
11. The device of claim 1, wherein the device further comprises a second polymeric matrix covering a portion of the first polymeric matrix, wherein the second polymeric matrix is impermeable to the volatile bases generated by decomposing food.
12. The device of claim 11, wherein the second polymeric matrix covers all of the first polymeric matrix except for a thin strip.
13. The device of claim 1, wherein the device further comprises a polymeric resin disposed within the first polymeric matrix.
14. The device of claim 1, wherein the device further comprises an acidic material disposed within the first polymeric matrix.
15. The device of claim 14, wherein the acidic material is a hydrated alumina, a zeolite, or phosphoric acid.
16. The device of claim 1, wherein the device is adapted for inclusion in a food package.
17. The device of claim 1, wherein the substrate comprises paper, plastic, cotton, flax, resin, glass, fiber glass, or fabric.
18. The device of claim 1, wherein the device consists of materials suitable for use with food.

19. A method of making an indicator device, comprising:
forming a solution of an indicator compound, a solvent, and an acid;
adding a silane monomer material to the solution;
disposing the solution on a substrate; and
polymerizing the silane monomer material on the substrate to form a silica matrix, wherein the indicator compound is disposed within the silica matrix.
20. A method of detecting spoiled frozen food, comprising:
exposing an indicator device to frozen food, the indicator device comprising a substrate and an indicator compound disposed on the substrate, wherein the indicator compound is colorimetrically responsive at temperatures below 0°C to volatile bases generated by spoiled frozen food; and
visually inspecting the device to determine if the food is spoiled by observing if the indicator compound has changed color.
21. The method of claim 20, wherein the indicator device further comprises an amine-impermeable polymeric matrix over the indicator compound and wherein the method further comprises
removing a portion of the amine-impermeable polymeric matrix to expose the indicator compound.
22. The method of claim 21, wherein the method further comprises
determining the amount of decomposition of the food by visually observing the amount of diffusion in a color change of the indicator compound adjacent the portion of the amine-impermeable polymeric matrix which was removed.
23. A food package for use with a food product, comprising:
packaging for a food product; and
an indicator device according to claim 1, associated with the packaging so as to be exposed to volatile bases emitted from the food product.

24. The food package of claim 23, comprising two or more indicator devices according to claim 1, each of the indicator devices having a different amount of indicator compound or having a different amount of acid provided with the indicator compound.

25. The food package of claim 23, wherein the food product is frozen red meat, pork, poultry, processed meat products, or seafood.

26. A method for detecting the presence of an unwanted amine-producing biological agent on a food product, comprising:

 exposing an indicator device to the food product, the indicator device comprising a substrate and an indicator compound disposed on the substrate, wherein the indicator compound is colorimetrically responsive to volatile bases emitted by the unwanted amine-producing biological agent; and

 visually inspecting the device to determine if the food product contains the unwanted biological agent by observing if the indicator compound has changed color.

27. The method of claim 26, wherein the indicator device further comprises an amine-impermeable polymeric matrix over the indicator compound and wherein the method further comprises

 removing a portion of the amine-impermeable polymeric matrix to expose the indicator compound.

28. The method of claim 27, wherein the method further comprises
 determining the amount of biological agent on the food product by visually observing the amount of diffusion in a color change of the indicator compound adjacent to the portion of the amine-impermeable polymeric matrix that was removed.

29. The method of claim 26, wherein the food product is grain and the unwanted biological agent is smut.

30. An indicator device, comprising:
a substrate; and
an indicator compound disposed on the substrate, the indicator compound
being colorimetrically response, without water mediation, to volatile bases generated
by food decomposition.

1/2

FIG. 1

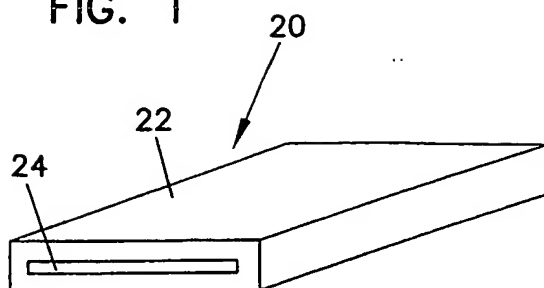


FIG. 2

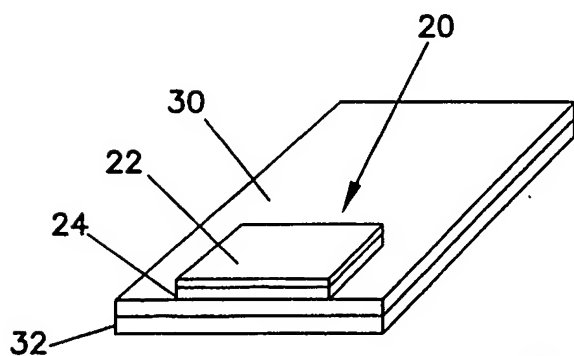
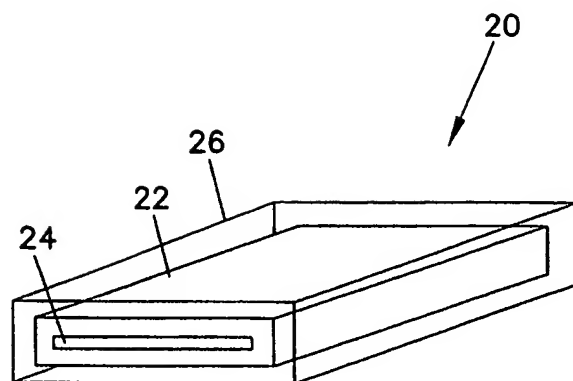


FIG. 5

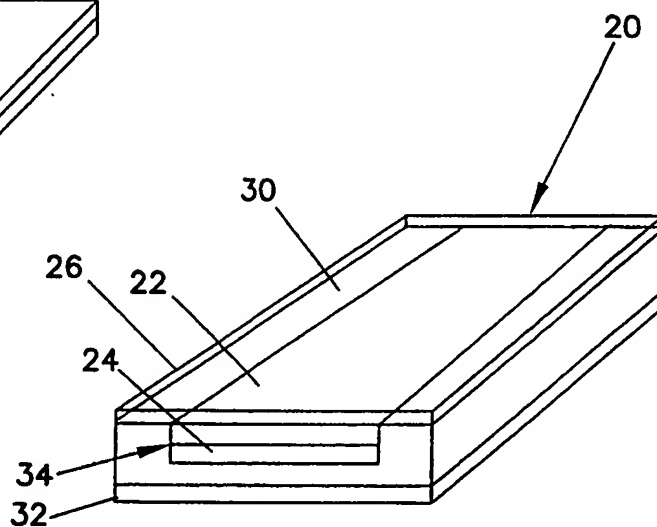
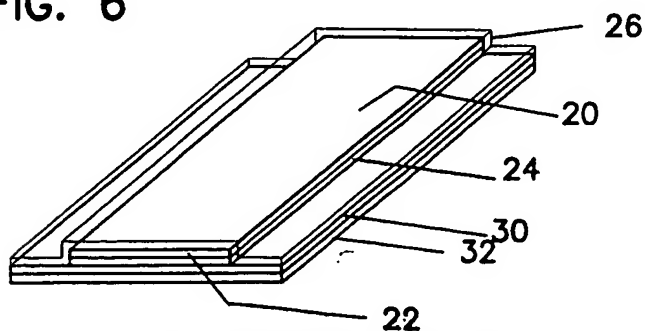


FIG. 7

FIG. 6



SUBSTITUTE SHEET (RULE 26)

2/2

FIG. 3A

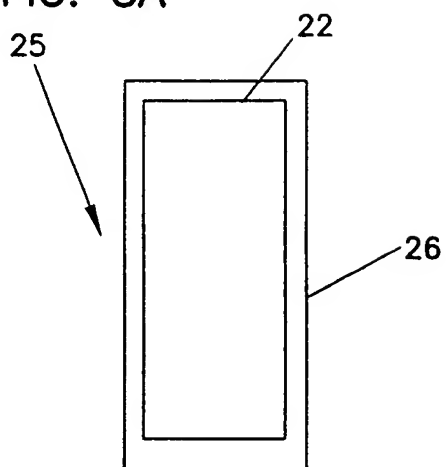


FIG. 3B

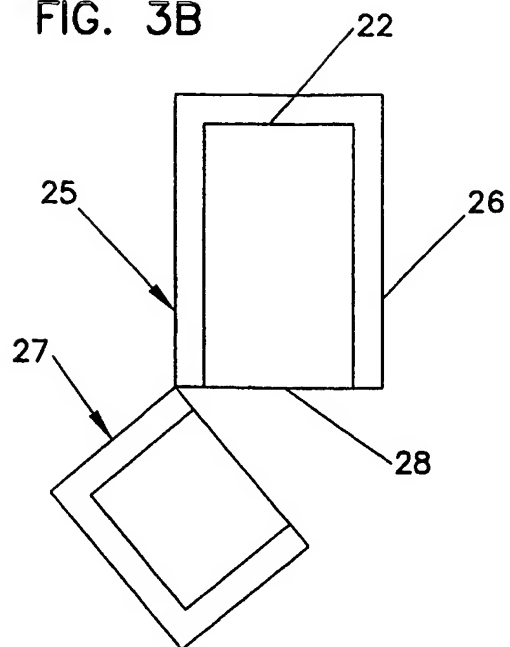


FIG. 3C

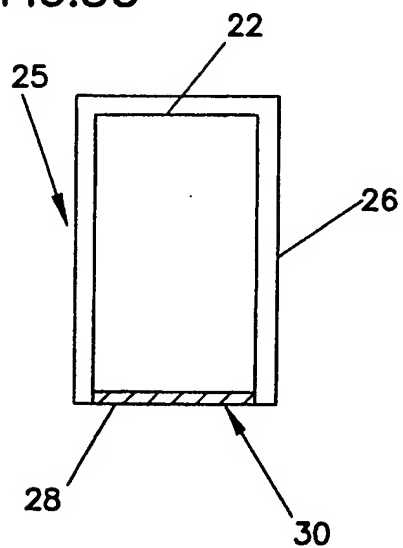


FIG. 3D

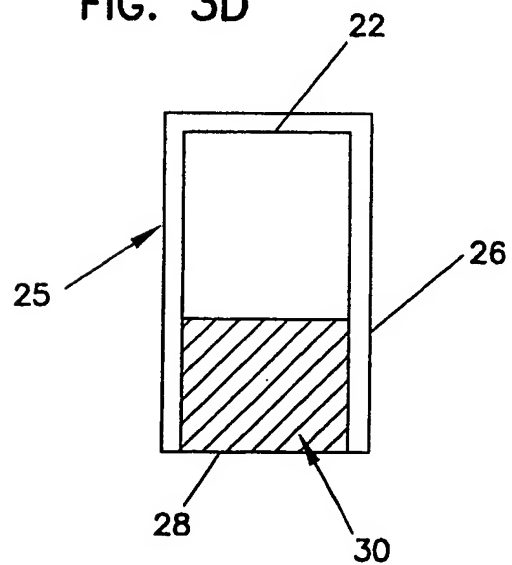
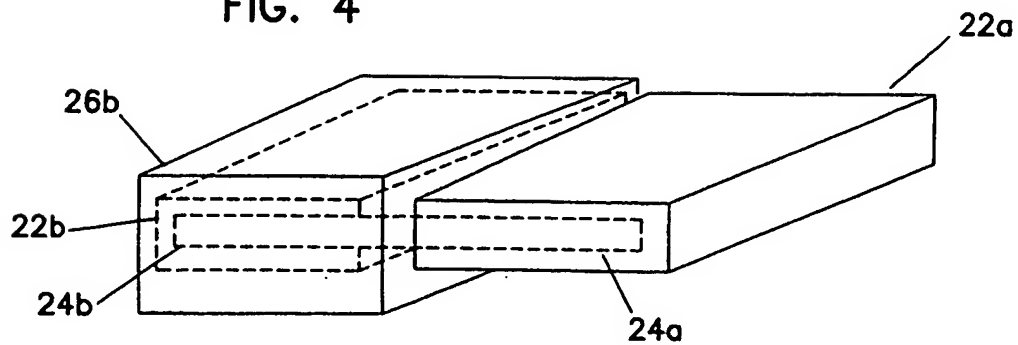


FIG. 4



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/14780

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N31/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 449 798 A (AVL MEDICAL INSTR AG) 2 October 1991 see column 5 - column 6; claims 1,2,7,10; example 2	1-30
X	DE 195 22 610 C (UNIV SCHILLER JENA) 5 December 1996 see the whole document	1-15,17, 19,30
X	EP 0 193 036 A (SIEMENS AG) 3 September 1986 see the whole document	1-6,17, 30
X	US 5 183 763 A (MALLOW WILLIAM A ET AL) 2 February 1993 see the whole document	1-9,30
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search

3 December 1998

Date of mailing of the international search report

21/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hart-Davis, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/14780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 348 358 A (MCKEE ELMER S ET AL) 7 September 1982 see example 4	1-6, 17, 30
X	US 5 501 836 A (MYERSON JOEL) 26 March 1996 see the whole document	19
A	WO 93 15403 A (BRITISH TECH GROUP) 5 August 1993 see the whole document	1, 16, 18, 20, 23, 30

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/14780

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0449798	A	02-10-1991	AT 394906 B	27-07-1992
			AT 71390 A	15-12-1991
			JP 4215929 A	06-08-1992
			US 5407829 A	18-04-1995
DE 19522610	C	05-12-1996	NONE	
EP 0193036	A	03-09-1986	DE 3506676 A	28-08-1986
			CA 1276532 A	20-11-1990
			DE 3689489 D	17-02-1994
			JP 61196204 A	30-08-1986
			US 4863694 A	05-09-1989
			US 4752447 A	21-06-1988
US 5183763	A	02-02-1993	EP 0485575 A	20-05-1992
			JP 5500863 T	18-02-1993
			WO 9119192 A	12-12-1991
			US 5322797 A	21-06-1994
US 4348358	A	07-09-1982	CA 1157751 A	29-11-1983
			DE 3137756 A	01-07-1982
			GB 2084725 A,B	15-04-1982
			JP 1608501 C	28-06-1991
			JP 2035940 B	14-08-1990
			JP 57086049 A	28-05-1982
US 5501836	A	26-03-1996	US 5608006 A	04-03-1997
WO 9315403	A	05-08-1993	AU 671613 B	05-09-1996
			AU 3363393 A	01-09-1993
			CA 2126694 A	05-08-1993
			EP 0623212 A	09-11-1994
			JP 7503539 T	13-04-1995
			NZ 246660 A	27-07-1997
			US 5663072 A	02-09-1997



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 31/22	A1	(11) International Publication Number: WO 99/04256 (43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14780 (22) International Filing Date: 16 July 1998 (16.07.98) (30) Priority Data: 60/052,674 16 July 1997 (16.07.97) US (71) Applicant (for all designated States except US): THE GOVERNMENT OF THE UNITED STATES OF AMERICA, re presented by THE SECRETARY, DEPARTMENT OF HEALTH AND HUMAN SERVICES [US/US]; Suite 325, 6011 Executive Boulevard, Rockville, MD 20852 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MILLER, Dwight, W. [US/US]; 2901 Dan Road, Pine Bluff, AR 71602 (US). WILKES, Jon, G. [US/US]; 621 Cumberland #1, Little Rock, AR 72207 (US). CONTE, Eric, D. [US/US]; 1080 St. Andrews Circle, Bowling Green, KY 42103 (US). (74) Agent: MUELLER, Douglas, P.; Merchant, Gould, Smith, Edell, Welter & Schmidt, P.A., 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402-4131 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i> Date of publication of the amended claims: 29 April 1999 (29.04.99)
(54) Title: FOOD QUALITY INDICATOR DEVICE (57) Abstract <p>A food quality indicator device comprising an indicator compound provided on a substrate. The indicator compound changes color due to the presence of volatile compounds, such as volatile bases, in spoiled food, even when the food is frozen. Alternatively, the indicator compound detects the presence of an unwanted amine-producing biological agent, such as bacteria or fungi. The indicator compound is typically contained within a polymeric matrix disposed on the substrate. Examples of suitable indicator compounds include halogenated azo dyes, sulfonated xanthene dyes, and sulfonated hydroxy-functional triphenylmethane dyes.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

AMENDED CLAIMS

[received by the International Bureau on 23 February 1999 (23.02.99);
original claims 17-21 amended; new claims 31-34 added (5 pages)]

1. An indicator device, comprising:
a substrate; and
an indicator compound disposed on the substrate, the indicator compound
5 being colorimetrically responsive at temperatures below 0°C to volatile bases
generated by food decomposition,
wherein the indicator device is adapted for use with food.
2. The device of claim 1, wherein the indicator compound comprises a
10 compound with a color transition in a range from about pH 1.0 and about pH 6.0.
3. The device of claim 2, wherein the indicator compound comprises a
compound with a color transition in a range from about pH 2.5 and about pH 5.0.
- 15 4. The device of claim 1, wherein the indicator compound comprises a
compound with one or more acidic functional groups in the absence of amino or
alkylamino functional groups, wherein at least one of the one or more acidic
functional groups is -COOH, -SO₃, -S(O₂)O-, or salts thereof.
- 20 5. The device of claim 1, wherein the indicator compound is a halogenated
xanthene dye, a sulfonated azo dye, or a sulfonated hydroxy-functional
triphenylmethane dye.
6. The device of claim 5, wherein the indicator compound is Bromophenol
25 Blue, Phloxine B, Rose Bengal, Congo Red, or Metanil Yellow.
7. The device of claim 1, wherein the device further comprises a first polymeric
matrix coated on the substrate and the indicator compound is disposed within the
first polymeric matrix.
30
8. The device of claim 7, wherein the first polymeric matrix comprises a
silicon-containing matrix.

9. The device of claim 7, wherein the first polymeric matrix is formed by an acid catalyzed polymerization of a monomer material.
- 5 10. The device of claim 9, wherein the monomer material comprises a tetraalkoxysilane, an alkyl trialkoxysilane, or a mixture thereof.
11. The device of claim 1, wherein the device further comprises a second polymeric matrix covering a portion of the first polymeric matrix, wherein the
10 second polymeric matrix is impermeable to the volatile bases generated by decomposing food.
12. The device of claim 11, wherein the second polymeric matrix covers all of the first polymeric matrix except for a thin strip.
- 15 13. The device of claim 7, wherein the device further comprises a polymeric resin disposed within the first polymeric matrix.
14. The device of claim 7, wherein the device further comprises an acidic
20 material disposed within the first polymeric matrix.
15. The device of claim 14, wherein the acidic material is a hydrated alumina, a zeolite, or phosphoric acid.
- 25 16. The device of claim 1, wherein the device is adapted for inclusion in a food package.
17. The device of claim 1, wherein the substrate comprises paper, plastic, cotton, flax, resin, glass, fiber glass, or fabric.
- 30 18. The device of claim 1, wherein the device consists of materials suitable for use with food.

AMENDED SHEET (ARTICLE 19)

19. A method of making an indicator device that is adapted for use with food, comprising:
- forming a solution of an indicator compound, a solvent, and an acid;
 - 5 adding a silane monomer material to the solution;
 - disposing the solution on a substrate; and
 - polymerizing the silane monomer material on the substrate to form a silica matrix, wherein the indicator compound is disposed within the silica matrix.
- 10 20. A method of detecting spoiled frozen food, comprising:
- exposing an indicator device to frozen food, the indicator device comprising a substrate and an indicator compound disposed on the substrate, wherein the indicator compound is colorimetrically responsive at temperatures below 0°C to volatile bases generated by spoiled frozen food; and
 - 15 visually inspecting the device to determine if the food is spoiled by observing if the indicator compound has changed color.
21. The method of claim 20, wherein the indicator device further comprises an amine-impermeable polymeric matrix over the indicator compound and wherein the
- 20 method further comprises
- removing a portion of the amine-impermeable polymeric matrix to expose the indicator compound.
22. The method of claim 21, wherein the method further comprises
- 25 determining the amount of decomposition of the food by visually observing the amount of diffusion in a color change of the indicator compound adjacent the portion of the amine-impermeable polymeric matrix which was removed.
23. A food package for use with a food product, comprising:
- 30 packaging for a food product; and
- an indicator device according to claim 1, associated with the packaging so as to be exposed to volatile bases emitted from the food product.

24. The food package of claim 23, comprising two or more indicator devices according to claim 1, each of the indicator devices having a different amount of indicator compound or having a different amount of acid provided with the indicator compound.

25. The food package of claim 23, wherein the food product is frozen red meat, pork, poultry, processed meat products, or seafood.

26. A method for detecting the presence of an unwanted amine-producing biological agent on a food product, comprising:

exposing an indicator device to the food product, the indicator device comprising a substrate and an indicator compound disposed on the substrate, wherein the indicator compound is colorimetrically responsive to volatile bases emitted by the unwanted amine-producing biological agent; and visually inspecting the device to determine if the food product contains the unwanted biological agent by observing if the indicator compound has changed color.

27. The method of claim 26, wherein the indicator device further comprises an amine-impermeable polymeric matrix over the indicator compound and wherein the method further comprises

removing a portion of the amine-impermeable polymeric matrix to expose the indicator compound.

28. The method of claim 27, wherein the method further comprises determining the amount of biological agent on the food product by visually observing the amount of diffusion in a color change of the indicator compound adjacent to the portion of the amine-impermeable polymeric matrix that was removed.

29. The method of claim 26, wherein the food product is grain and the unwanted biological agent is smut.
30. An indicator device, comprising:
5 a substrate; and
an indicator compound disposed on the substrate, the indicator compound being colorimetrically response, without water mediation, to volatile bases generated by food decomposition,
wherein the indicator device is adapted for use with food.
- 10 31. An indicator device, comprising:
a substrate; and
an indicator compound disposed on the substrate, the indicator compound being colorimetrically responsive at temperatures below 0°C to volatile acids
15 generated by food decomposition,
wherein the indicator device is adapted for use with food.
32. The device of claim 31, wherein the device further comprises a first polymeric matrix coated on the substrate and the indicator compound is disposed
20 within the first polymeric matrix.
33. The device of claim 32, wherein the device further comprises a basic material disposed within the first polymeric matrix.
- 25 34. A method of detecting spoiled frozen food, comprising:
exposing an indicator device to frozen food, the indicator device comprising a substrate and an indicator compound disposed on the substrate, wherein the indicator compound is colorimetrically responsive at temperatures below 0°C to volatile acids generated by spoiled frozen food; and
30 visually inspecting the device to determine if the food is spoiled by observing if the indicator compound has changed color.

AMENDED SHEET (ARTICLE 19)